

# Coupling between Smectic and Twist Modes in Polymer Intercalated Smectics

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## Abstract

We analyse the elastic energy of an intercalated smectic where orientationally ordered polymers with an average orientation varying from layer to layer are intercalated between smectic planes. The lowest order terms in the coupling between polymer director and smectic layer curvature are added to the smectic elastic energy. Integration over the smectic degrees of freedom leaves an effective polymer twist energy that has to be included into the total polymer elastic energy leading to a fluctuational renormalization of the intercalated polymer twist modulus. If the polymers are chiral this in its turn leads to a renormalization of the cholesteric pitch.

Recent elucidation of the structure of DNA - cationic lipid complexes [1, 2] has brought forth quite a few unsuspected features of this macromolecular aggregate. It appears that cationic lipids in the complex retain their preferred packing characterised by a multilamellar 3-D smectic order while the oppositely charged DNA gets intercalated in between the lipid bilayer smectic planes. The intercalated DNA appears to be packed with a 2-D smectic order of relatively small domain sizes that are probably coupled to the order in the neighboring intercalated DNA layers [2]. The careful X-ray diffraction studies leave no ambiguity as to the fact that both components of the complex - cationic lipids as well as DNA are ordered.

The ordering tendencies giving rise to this complex aggregate structure are due partly to the fairly well understood interactions between lipid bilayers in aqueous solutions where van der Waals attraction competes with electrostatic and hydration forces, augmented by entropic repulsion forces originating in elastic fluctuations of the lipid bilayers constrained to a multilamellar stack [3]. Similarly interactions between DNA molecules in the bulk that have only recently come under closer experimental as well as theoretical scrutiny, appear to be dominated by repulsive forces of electrostatic as well as hydration origin, this time too augmented through entropic mechanism very similar to the one operating in multilamellar lipid systems [4]. The interaction between the two constituents of the complex are probably dominated by the electrostatic attraction between DNA and cationic lipids possibly modified by elastic shape fluctuations of the DNAs intercalated between positively charged layers of lipids and possibly by the forces mediated by the lipid bilayer elasticity due to local deformations induced by the close proximity of intercalated DNA. More work is certainly needed to assess the relative importance of all these mechanisms in bringing about the stability of the DNA - cationic lipid complex.

Compared to the phases existing in the bulk the lipid subphase does not appear to be substantially modified. It has the same structural geometry as the one found with other lipids in the bulk. DNA is in this respect very much modified. At effective interhelical spacings found in the DNA - CL complex [2], DNA in the bulk would be either in the line hexatic phase or within the cholesteric phase [5]. Very little of this bulk order persists in intercalated DNA that is forced into effectively 2-D layers intercalated between lipid bilayers. The positional order does not change qualitatively if we consider only DNA intercalated within a single layer. They are both short ranged [2]. The orientational order is changed more drastically if the state of affairs in the bulk and in the DNA-CL complex are compared. It is nevertheless the apparent total absence of the cholesteric order in the complex that seems to us the most baffling. Apart from very tentative statements [6] that cholesteric structures of extremely large pitch ( $\sim$  mm) can sometimes be detected in the complex the chiral nature of the DNA molecule makes no imprint on the structure of this macromolecular aggregate.

It is our goal in this contribution to investigate the interaction between orientational order of intercalated polymers and the smectic degrees of freedom of intercalating lipid bilayers. We propose a simple theory of the effect that the coupling between polymer (*i.e.* DNA) orientational ordering within the intercalated layers and smectic order of these layers can have on the effective twist elastic constant of the polymer layers. If in addition the intercalated polymers are chiral, this theory for the first time introduces a comprehensive mechanism for coupling between smectic and cholesteric degrees of freedom leading to a fluctuational renormalization of the cholesteric pitch of the polymer subsystem.

*Model* We will consider a simplified model of an intercalated smectic

the director of the polymers  $\mathbf{n}(n; \boldsymbol{\rho})$  within an intercalated layer is a constant. We introduced  $n$  as the height index of the layer (layers are assumed to have the average positions at  $z_n = n \times d$  where  $d$  is the average layer - layer separation) while  $\boldsymbol{\rho} = (x, y)$  is the transverse radius vector. We have thus effectively limited ourselves to a mean-field approximation within a single layer.

We will construct an elastic free energy of this system, assuming a general dependence of the polymer director on the position i.e. height index  $n$ , of the layer. Since the polymer orientational order can interact with the curvature energy of each layer we first have to construct all the scalar invariants that can be composed with  $\mathbf{n}$  and the 2nd fundamental form of a single smectic layer.

If one defines the 2nd fundamental form of Gauss of the  $n$ -th layer with local displacement described within the Monge parametrization  $(x, y, \zeta_n(x, y))$  as

$$K_{ik}(n; \boldsymbol{\rho}) = \frac{\partial^2 \zeta_n(\boldsymbol{\rho})}{\partial x_i \partial x_k} \quad (1)$$

where the indices  $i, k$  can have values  $i, k = 1, 2$  with  $x_1 = x$  and  $x_2 = y$ , then the lowest order scalar invariants which can be built from the director  $\mathbf{n}$  and the tensor Eq.1 of that layer are three [8]

$$\begin{aligned} & K_{ii} K_{ik} n_i n_k \\ & K_{li} K_{ik} n_l n_k \\ & K_{ik} K_{lm} n_i n_k n_l n_m. \end{aligned} \quad (2)$$

Only two of these invariants are linearly independent if we ignore the terms containing Gaussian curvature. The curvature elastic energy of  $n$ -th surface, assuming that within each layer the director of the polymers is a constant  $\mathbf{n}(n; \boldsymbol{\rho}) = \mathbf{n}(n)$ , can be written as

$$\begin{aligned} H_n(K_{ik}; \mathbf{n}) &= \frac{1}{2} K_c \int (Tr K_{ik}(n; \boldsymbol{\rho}))^2 d^2 \boldsymbol{\rho} + \\ &+ \frac{1}{2} a \int K_{li}(n; \boldsymbol{\rho}) K_{ik}(n; \boldsymbol{\rho}) n_l(n) n_k(n) d^2 \boldsymbol{\rho} + \\ &+ \frac{1}{2} b \int K_{ik}(n; \boldsymbol{\rho}) K_{lm}(n; \boldsymbol{\rho}) n_i(n) n_k(n) n_l(n) n_m(n) d^2 \boldsymbol{\rho} \end{aligned} \quad (3)$$

In a stack of layers the total elastic energy is composed of curvature elastic energy Eq.3 and the deformation energy due to smectic dilations - compressions of the layers in the transverse direction, characterised by a smectic compressibility modulus  $\mathcal{B}$  [9]

$$H = \int H_n(K_{ik}; \mathbf{n}) dn + \frac{1}{2} \mathcal{B} \iint \left( \frac{\partial \zeta_n(\boldsymbol{\rho})}{\partial n} \right)^2 dn d^2 \boldsymbol{\rho} \quad (4)$$

The formal limits of this expression are well known and will not be discussed here. Introducing Fourier transform of the local displacement in the directions  $\boldsymbol{\rho}$  with wave vector  $\mathbf{Q}$  we obtain for the total smectic elastic energy the expression

$$H = \frac{1}{2} \sum \int dn \left[ (K_c Q^4 + a Q^2 (\mathbf{Q} \cdot \mathbf{n}(n))^2 + b (\mathbf{Q} \cdot \mathbf{n}(n))^4) |\zeta_n(\mathbf{Q})|^2 + \mathcal{B} \left( \frac{\partial \zeta_n(\mathbf{Q})}{\partial n} \right)^2 \right] =$$

where we have defined the operator  $\mathcal{H}(n, n'; \mathbf{Q})$  and used the shorthand  $\sum_{\mathbf{Q}} = \frac{S}{(2\pi)^2} \int d^2\mathbf{Q}$  with  $S$  being the area of the layer. The elastic energy expression Eq. 5 represents the final formalisation of our model. If the intercalated polymers are chiral we have to add to Eq. 5 the standard cholesteric elastic energy which depends in the lowest order only on the derivatives of the polymer director with respect to the stack index [9].

*Free energy of smectic fluctuations* We now proceed by integrating out the smectic fluctuations from the free energy defined through elastic Hamiltonian Eq.5 and thus obtaining an effective intercalated polymer free energy that will depend only on the director field of the polymers. We start by setting

$$\phi(n; \mathbf{Q}) = aQ^2 (\mathbf{Q}\mathbf{n}(n))^2 + b(\mathbf{Q}\mathbf{n}(n))^4 \quad (6)$$

and writing out explicitly the operator we introduced above Eq. 5

$$\mathcal{H}(n, n'; \mathbf{Q}) = \left( -\beta\mathcal{B}\frac{\partial^2}{\partial n^2} + \beta K_c Q^4 + \beta\phi(n; \mathbf{Q}) \right) \delta(n - n'), \quad (7)$$

which allows us to express the free energy corresponding to smectic elastic fluctuations as

$$\begin{aligned} \mathcal{F}(\mathbf{n}(n)) &= -kT \ln \Xi = -kT \ln \left( \Pi_{\mathbf{Q}} \int \cdots \int \mathcal{D}\zeta_n(\mathbf{Q}) \exp(-\beta H) \right) = \\ &= \frac{kT}{2} \sum_{\mathbf{Q}} \ln \text{Det} \mathcal{H}(n, n'; \mathbf{Q}). \end{aligned} \quad (8)$$

In order to get the part of the free energy that depends explicitly on the polymer director field, it is convenient to resort to the following representation of the free energy Eq.8

$$\begin{aligned} \mathcal{F}(\mathbf{n}(n)) &= \frac{kT}{2} \sum_{\mathbf{Q}} \text{Tr} \ln (\mathcal{H}(n, n'; \mathbf{Q})) = \\ &= \mathcal{F}_0 + \frac{1}{2} \sum_{\mathbf{Q}} \text{Tr} \phi(n; \mathbf{Q}) \int_0^1 d\mu \mathcal{G}_{\mu}(n, n'; \mathbf{Q}), \end{aligned} \quad (9)$$

where  $\mathcal{F}_0$  is the part of the free energy that does not contain  $\mathbf{n}(n)$  explicitly. The Green function  $\mathcal{G}_{\mu}(n, n'; \mathbf{Q})$  entering the above equation can be obtained as [10]

$$\left( -\beta\mathcal{B}\frac{\partial^2}{\partial n^2} + \beta K_c Q^4 + \mu\beta\phi(n; \mathbf{Q}) \right) \mathcal{G}_{\mu}(n, n'; \mathbf{Q}) = \delta(n - n'). \quad (10)$$

Introducing now  $\mathcal{G}_0(n, n'; \mathbf{Q}) = \mathcal{G}_0(|n - n'|; \mathbf{Q}) = \mathcal{G}_{\mu=0}(n, n'; \mathbf{Q})$  in the form

$$\mathcal{G}_0(n - n'; \mathbf{Q}) = \frac{1}{2} \sqrt{\frac{\mathcal{B}}{K_c}} Q^{-2} \exp \sqrt{\frac{K_c}{\mathcal{B}}} Q^2 |n - n'| \quad (11)$$

we can expand  $\mathcal{G}_{\mu}(n, n'; \mathbf{Q})$  perturbatively up to the first order in  $\phi(n; \mathbf{Q})$  thus obtaining the free energy to the second order in this quantity

Since the zero order Green function is obviously of short range we can expand the expression for the free energy Eq.12 for a slowly varying  $\phi(n; \mathbf{Q})$  field in a standard fashion, obtaining the following approximate form of the free energy

$$\begin{aligned} \mathcal{F}(\mathbf{n}(n)) &= \mathcal{F}_0 + \frac{1}{2} \sum_{\mathbf{Q}} \left[ \mathcal{G}_0(0; \mathbf{Q}) \int dn \phi(n; \mathbf{Q}) - \right. \\ &\quad - \frac{\beta}{2} \left( \int dt \mathcal{G}_0^2(t; \mathbf{Q}) \right) \int dn \phi^2(n; \mathbf{Q}) + \\ &\quad \left. + \frac{\beta}{4} \left( \int dt t^2 \mathcal{G}_0^2(t; \mathbf{Q}) \right) \int dn \left( \frac{\partial \phi(n; \mathbf{Q})}{\partial n} \right)^2 \right]. \end{aligned} \quad (13)$$

The summation over the Fourier space intends also integration over the different directions of the  $\mathbf{Q}$  vector. Denoting this orientational integration with  $\langle \dots \rangle_{\omega}$  it is easy to see that  $\langle \phi(n; \mathbf{Q}) \rangle_{\omega}$  as well as  $\langle \phi^2(n; \mathbf{Q}) \rangle_{\omega}$  do not depend on the orientational angles at all and are thus independent of the director field  $\mathbf{n}(n)$ . The dependence on the director field remains only in the derivative terms, i.e. terms of the form  $\left( \frac{\partial \phi(n; \mathbf{Q})}{\partial n} \right)^2$ . These terms contain

$$\frac{d(\mathbf{Q}\mathbf{n}(n))}{dn} = \mathbf{Q} \frac{d\mathbf{n}(n)}{dn} = \mathbf{Q}\dot{\mathbf{n}}(n) = \mathbf{Q} (\mathbf{n}(n) \times \boldsymbol{\Omega}(n)) \quad (14)$$

where  $\boldsymbol{\Omega}(n)$  is the vector of the “angular velocity” of rotation of the director from layer to layer. If the average normal to the layers is in the  $z$  direction than  $\boldsymbol{\Omega}(n) = (0, 0, \Omega_z(n))$ , also  $\dot{\mathbf{n}}(n)$  is within each layer and in direction perpendicular to  $\mathbf{n}(n)$  with magnitude  $|\dot{\mathbf{n}}(n)| = \Omega_z(n)$ . As can be easily seen, the only terms that survive the integration  $\langle \dots \rangle_{\omega}$  and still depend on the director field are those depending quadratically on  $|\dot{\mathbf{n}}(n)|$ . From the free energy Eq.13 these terms can be obtained in the form

$$\mathcal{F}(\mathbf{n}(n)) = \mathcal{F}_0(a, b) + \frac{\beta}{8} \frac{S}{4\pi} \int_0^\infty Q^9 dQ \left( \int dt t^2 \mathcal{G}_0^2(t; \mathbf{Q}) \right) \left( (a+b)^2 + \left( \frac{b}{2} \right)^2 \right) \int |\dot{\mathbf{n}}(n)|^2 dn, \quad (15)$$

where  $\mathcal{F}_0(a, b)$  is the part of the free energy that after the  $\langle \dots \rangle_{\omega}$  integration does not depend explicitly on the director any more. Evaluating the last integral over  $Q$  and taking into account the fact that the minimal value of  $Q$  is set by the domain size, assumed to be a square of side  $l$ , while the maximal value is set by the molecular dimension  $a$ , we obtain finally

$$\begin{aligned} \mathcal{F}(\mathbf{n}(n)) &= \mathcal{F}_0(a, b) + \frac{\beta}{512\pi} \left( \frac{\mathcal{B}}{K_c} \right)^{5/2} \left( (a+b)^2 + \left( \frac{b}{2} \right)^2 \right) \ln \frac{l}{a} \int |\dot{\mathbf{n}}(n)|^2 dn = \\ &= \mathcal{F}_0(a, b) + \frac{K_{st}}{2} \int |\dot{\mathbf{n}}(n)|^2 dn \end{aligned} \quad (16)$$

Clearly for this geometry  $K_{st}$  is the additional twist elastic constant of intercalated polymers, stemming from the smectic interactions between layers of orientationally ordered polymer molecules. Thus we see that in an intercalated smectic the smectic interactions tend to renormalize the twist elastic modulus of intercalated oriented polymers to

$$K_{st} = K_{st} + \frac{\beta}{512\pi} \left( \frac{\mathcal{B}}{K_c} \right)^{5/2} \left( (a+b)^2 + \left( \frac{b}{2} \right)^2 \right) \ln \frac{l}{a} \quad (17)$$

This renormalization is of purely fluctuational origin. If the polymers are in addition chiral, the renormalization of the twist modulus obviously leads to unwinding of the cholesteric pitch of the intercalated polymers to a new equilibrium value of

$$P \longrightarrow P \left( 1 + \frac{\beta}{256\pi K_2} \left( \frac{\mathcal{B}}{K_c} \right)^{5/2} \left( (a+b)^2 + \left( \frac{b}{2} \right)^2 \right) \ln \frac{l}{a} \right). \quad (18)$$

*Discussion* The mean - field model introduced above led in a very straightforward way to a renormalization of the twist modulus of intercalated polymers. The effect itself is a very intuitive one. If there exists a deformational “easy axis” within each smectic layer, which according to Eq.5 represents a deformational wave whose direction is perpendicular to  $\mathbf{n}(n)$  within a single layer, the smectic compressibility term would tend to twist the directors of the neighboring layers towards a colinear position. This would introduce a coupling term  $(\mathbf{n}(n) - \mathbf{n}(n+1))^2$  in the free energy of two neighboring layers. The continuum version of this effect would lead exactly to Eq.16.

The coupling constants  $a$  and  $b$ , *c.f.* Eq.3, between the orientational ordering of intercalated polymers and effective elastic properties of the layers depend in general on the orientational order parameter of the polymer chain  $\mathcal{S}$ , the elastic modulus of the chains defined as  $kT\mathcal{L}_p$  where  $\mathcal{L}_p$  is the persistence length and the polymer surface density  $\rho$ . The orientational order parameter of the polymer chains is defined through the 2-D orientational tensor  $\sigma_{ik}$  of the intercalated chains as  $\sigma_\alpha = \frac{\rho}{2}(1 \pm \mathcal{S})$ , where  $\alpha$  is the index of the two eigenvalues [11]. For  $\mathcal{S}$  close to 1, *i.e.* close to complete orientational order where all the chains point in the same direction, the scaling form for  $a$  and  $b$  should be

$$a, b \sim kT \mathcal{S} \frac{\mathcal{L}_p}{\ell_\perp}, \quad (19)$$

where  $\ell_\perp$  is the separation between the chains perpendicular to their long axis. This is the form appropriate for our assumption of complete ordering of chains within each smectic layer.

We can now assess the magnitude of the contribution of smectic modes to the twist elastic modulus of the smectic layers. Assuming the scaling Eq. 19 for constants  $a$  and  $b$  we obtain

$$K_{st} \sim (kT)^{-1} \left( \frac{\mathcal{B}}{K_c} \right)^{5/2} \left( kT \mathcal{S} \frac{\mathcal{L}_p}{\ell_\perp} \right)^2 \quad (20)$$

times an unknown numerical constant presumably on the order of 10. In the units used in Eq. 5  $\frac{\mathcal{B}}{K_c}$  is dimensionless. Since the dominant interactions determining  $\mathcal{B}$  are electrostatic attractions between DNA and cationic lipid headgroups the smectic modulus has to be quite large while  $\frac{\mathcal{L}_p}{\ell_\perp}$  is on the order of 10, the modification of the twist modulus implied by Eq. 17 thus has to be enormous. If the intercalated polymers are chiral it would thus come as no surprise if the effective cholesteric pitch surviving in this system would be orders of magnitude larger than in the pure polymer system [6].

We have not included the possible direct modification of the chiral interactions by smectic fluctuations in this analysis, an effect that would act in the direction opposite to the smectic fluctuation renormalization of the polymer twist modulus. As this effect would tend to make the effective pitch smaller, which apparently has never been observed in this system, we assume

pitch in such a system, if the polymers themselves are chiral. We propose this as the primary reason why no cholesteric structures have been observed in the DNA-CL system.

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*Figures* Fig.1. A schematic representation of a part of a polymer intercalated smectic system. The smectic layers are not shown explicitly. The direction of the intercalated polymers changes from layer to layer. It has been arbitrarily assumed to change by  $\frac{\pi}{4}$  between two neighboring layers. The smectic interactions tend to orient the neighboring polymer layers in a parallel direction.

## References

- [1] D.D. Lasič, H.H. Strey, M.C.A. Stuart, R. Podgornik and P.M. Frederik, *J. Amer. Chem. Soc.* 119, 832-833 (1997).
- [2] J.O. Rädler, I. Koltover, T. Salditt, C.R. Safinya, *Science* 275, 810-814 (1997).
- [3] V.A. Parsegian and R.P. Rand, in *Structure and Dynamics of Membranes*, Handbook of Biological Physics, Vol. 1, Eds. R. Lipowsky and E. Sackmann, (Elsevier) 643 - 690 (1995).
- [4] H.H. Strey, D.C. Rau, V.A. Parsegian and R. Podgornik, *Phys.Rev.Lett.* 78 895-898 (1997)
- [5] R. Podgornik, H.H. Strey, K. Gawrisch, D.C. Rau, A. Rupprecht and V.A. Parsegian, *Proc. Natl. Acad. Sci.* 93, 4261-4266 (1996).
- [6] J.O. Rädler, personal communication (1997).
- [7] J. Yang, J. Mou and Z. Shao, *FEBS Letters* 301, 173-175 (1995).
- [8] F. David, E. Guitter and L. Peliti, *J. Physique* 48, 2059-2066 (1987).
- [9] P.G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, (Oxford) (1993).
- [10] P.M. Chaikin and T.C. Lubensky, *Principles of Condensed Matter*, (Cambridge) (1995).
- [11] R. Podgornik, *Phys.Rev. E* 54, 5268-5277 (1996).